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(PATENT)

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of:  
Poul E. Nielsen et al.

Application No.: Not Yet Assigned

Filed: Concurrently Herewith

Art Unit: N/A

For: PROCESS FOR PREPARATION OF  
METHANOL

Examiner: Not Yet Assigned

**CLAIM FOR PRIORITY AND SUBMISSION OF DOCUMENTS**

MS Patent Application  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

Applicant hereby claims priority under 35 U.S.C. 119 based on the following  
prior foreign application filed in the following foreign country on the date indicated:

<u>Country</u>	<u>Application No.</u>	<u>Date</u>
Denmark	PA 2003 00529	April 7, 2003

Application No.: Not Yet Assigned

Docket No.: H0610.0361/P361

In support of this claim, a certified copy of the said original foreign application is filed herewith.

Dated: March 23, 2004

Respectfully submitted,

By 

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# Kongeriget Danmark

Patent application No.: PA 2003 00529

Date of filing: 07 April 2003

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Title: Fremgangsmåde til fremstilling af methanol.

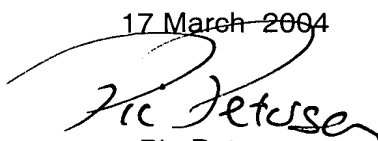
IPC: C 07 C 29/151

This is to certify that the attached documents are exact copies of the above mentioned patent application as originally filed.



**Patent- og Varemærkestyrelsen**  
Økonomi- og Erhvervsministeriet

17 March 2004

  
Pia Petersen



**PATENT- OG VAREMÆRKESTYRELSEN**



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HABS/AKN

**Modtaget**

**-7 APR. 2003**

**PVS**

**Process for the Preparation of Methanol**

-7 APR. 2003

## DESCRIPTION

PVS

5 The present invention relates to conversion of synthesis gas into methanol at condensing conditions. In particular, the invention is a methanol preparation process being carried out in a slurry reactor, wherein condensed methanol product is utilised as suspension medium for a catalyst being active in the methanol synthesis reactions.

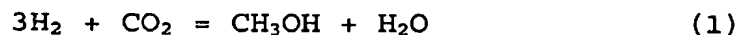
10 Synthesis gas is any gas composition comprising hydrogen and carbon dioxide and/or carbon monoxide being able to establish condensing conditions.

## BACKGROUND OF INVENTION

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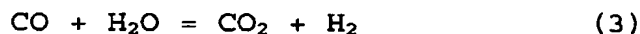
Heterogeneous methanol synthesis is in today's practice carried out by reacting carbon oxides with hydrogen in the presence of copper-based catalysts according to the following equations:

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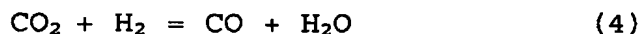


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The methanol synthesis catalyst also catalyses the Water Gas Shift (WGS) reaction,



and the Reverse Water Gas Shift (RWGS) reaction,



30

In large-scale methanol plants, the gas phase synthesis reactor is typically a cooled tubular reactor or a multistage adiabatic reactor. The typical temperature range for metha-

nol synthesis is 200-300°C. Cooled reactors normally operate at approximately 250°C, whereas adiabatic reactors typically operate between 220°C and 300°C. The reaction to methanol is strongly exothermic, and efficient heat removal is a problem. This limits the range of composition of the feed gas that can be treated in a tubular reactor, for example CO rich gases are very exothermic and difficult to process. Inefficient heat removal leads to hot zones in the reactor, and the catalyst may thus deactivate faster. By-product formation is promoted at high temperatures. For example the production of ethanol and ketones increases with temperature. Alcohols and ketones are difficult to separate from methanol-water mixtures due to the formation of azeotropes.

With respect to pressure, the typical operating pressure for methanol synthesis is within 50-100 bar. Cooled reactors typically operate at 50 bar whereas adiabatic reactors generally operate at a higher pressure, typically around 80 bar.

The synthesis gas used in methanol synthesis can be derived from natural gas either by steam reforming of natural gas or by autothermal reforming.

The conversion to methanol is determined by the thermodynamic equilibrium constant. In today's practice this typically results in effluent concentrations in the range between 4% and 10% in all cases with only a partial conversion of the carbon oxides. Thus, to obtain maximum use of the produced synthesis gas, a recycle of the unconverted gas is necessary. A high recycle ratio ensures a high con-

version. A high recycle flow through the reactor increases the compression cost. Before recycling, the effluent gas is cooled and separated from the liquid product. The effluent gas can be enriched in hydrogen by employing, for example, membrane separation. The enriched gas is recycled to the reactor. The inert level (notably methane) is kept under control by a purge.

Condensing conditions are defined as the operating conditions of a methanol synthesis, wherein the methanol saturation pressure is reached before the reaction equilibrium of the synthesis gas composition is reached. The critical temperature for methanol is 240°C. Non-condensing and condensing conditions are separated for a given synthesis gas composition at a given operating temperature by a pressure,  $P_{lim}$ . Above this pressure, condensing conditions are present whereas below this pressure, non-condensing conditions are present (see FIG.).

As the methanol saturation pressure increases with temperature and the equilibrium methanol pressure decreases with temperature,  $P_{lim}$  increases with temperature. Above the saturation curve, the total mole fraction of methanol in the equilibrium mixture is depicted as a dashed line.

The characteristic of a preferred synthesis gas composition is a low  $P_{lim}$ . The typical condensing conditions for preferred synthesis gas compositions is at temperatures 190-240°C and at pressures 60-140 bar.

The original invention of the slurry reactor was made by Chem Systems and is described in US Patent No. 3,888,896.

Herein a preparation process is described using an inert organic liquid such as pseudocumene as the slurry medium.

A series of patents from Air Products (US Patent Nos. 4,628,066, 4,766,154, 4,910,277, 5,179,129 and 5,284,878) describe the application of a slurry reactor for methanol synthesis. These applications are characterised by the suspension of the methanol catalyst in an inert liquid, typically a high-molecular-weight hydrocarbon. Only partial conversion of methanol is considered here, as the reaction conditions are given as 30-100 bar and 210-250°C.

The finely divided catalyst must be separated from the liquid product. U.S. Patent No. 5,520,890 by Den Norske Stats Oljeselskap A.S. describes an apparatus for solid-liquid slurry treatment. The patent provides a solution for the separation of fine catalyst particles from the liquid by operation in tubes including filtrate zones.

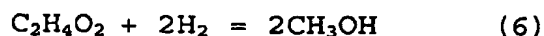
JP Patent No. 57126434 describes a methanol preparation method from CO and/or CO<sub>2</sub> in the presence of a water-soluble, basic substance where water is used as slurry medium.

A completely different approach to methanol synthesis from alkyl formates was first described by J.A. Christiansen in US Patent No. 1,302,011. This approach is also described in US Patent No. 5,384,335 and consists of two distinct steps: *First step:* Carbonylation of methanol to methyl formate, HCOOCH<sub>3</sub> (= C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>), in a basic medium e.g.





Second step: Reduction of methyl formiate to methanol on a Cu-based catalyst



5 Various solvents are described including the use of methanol as a solvent. The conditions under which the above reactions take place differ significantly from the conditions applied in industrial methanol synthesis. Reaction 5 requires a temperature much lower than 200°C whereas reaction  
10 6 is preferably carried out at much higher temperatures. In some processes the reactions are actually carried out in separate reaction vessels.

The most important difference between the above process and  
15 the industrial methanol synthesis is the role of CO<sub>2</sub>. In the above process CO<sub>2</sub> acts as a poison for reaction 5, whereas in the heterogeneous synthesis of methanol (reaction 1) CO<sub>2</sub> is a necessary reactant. H<sub>2</sub>O also acts as a poison in the above process.

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A conversion not limited by the thermodynamic equilibrium can be obtained in the case of a methanol product removal under synthesis. US Patent No. 5,262,443 to Haldor Topsoe A/S describes such a process where methanol synthesis is  
25 carried out under condensing conditions in a fixed bed in a cooled reactor. Methanol condensing conditions are characterised as having a temperature below the critical temperature of methanol, 240°C. In addition the methanol partial pressure calculated from the gas phase equilibrium constant  
30 is larger than the boiling pressure of methanol at the actual temperature. The process is most conveniently carried out with a stoichiometric synthesis gas very rich in CO.

The removal of heat in the tubular reactor is one of the key problems of such a process. The reaction rate is very high since the most preferred synthesis gas contains 31% CO, 2% CO<sub>2</sub> and 67% H<sub>2</sub> at a pressure of approximately 100 bar.

In contrast to the above discussed prior art, the present invention is a preparation method for methanol at condensing reaction conditions wherein the methanol catalyst is suspended in methanol and water and wherein the directly condensed product (primarily methanol and water) continuously makes up the suspension medium for the methanol catalyst. At condensing conditions, produced methanol at equilibrium can be condensed and high conversions can be obtained. Simultaneously, the methanol suspension offers a better possibility for controlling the reaction heat since produced methanol is absorbed uniformly within the liquid. The efficient temperature control is necessary to reduce by-product formation and to minimise deactivation of the catalyst.

#### SUMMARY OF THE INVENTION

The present innovation is a liquid phase process for the production of methanol in a slurry-bed reactor. In this process, methanol product is utilised as a catalyst suspension liquid medium. This process exploits the condensing conditions to produce methanol. The methanol partial pressure (calculated from the gas phase equilibrium constant) is larger than the boiling pressure of methanol at the given temperature resulting in a condensation of the methanol product. Synthesis gas conversion is thereby not lim-

ited by equilibrium. The equilibrium and saturation composition is affected by temperature. For an increase in temperature, the pressure needs to be increased to obtain condensing conditions.

5

In one embodiment of the present invention, the synthesis gas is compressed to a pressure higher than  $P_{lim,t}$  and fed to the slurry methanol reactor operated at a temperature,  $t$ ; the synthesis gas is converted in contact with a catalyst active in methanol synthesis to a degree, where condensing conditions are obtained resulting in a directly condensed methanol product and an effluent synthesis gas saturated with methanol; the directly condensed methanol product (primarily methanol, water and  $CO_2$ ) constitutes the suspension liquid medium for the catalyst active in methanol synthesis; the effluent synthesis gas stream rich in methanol is cooled down and separated to attain further product retrieval. The directly condensed methanol product used as suspension liquid is conventionally separated and recovered from the solid catalyst particles e.g. by filtration. The solid catalyst particles are recycled to the slurry reactor. The resulting methanol product is obtained from both the directly condensed methanol product and the retrieved methanol from the effluent synthesis gas.

25

In the known liquid phase methanol processes, the liquid suspension medium is an inert hydrocarbon liquid and an additional liquid phase is introduced into the system. This additional liquid phase must be separated from the product methanol. By the inventive methanol process, there is no need for a liquid phase separation stage, since the product and suspension liquid is the same component, i.e. methanol.

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Hence, a high purity methanol product will be withdrawn from the reaction, and contamination of high molecular weight hydrocarbons can be avoided.

5 The liquid phase slurry reactor represents a solution to the heat removal problem in the known methanol process. The reactions for methanol formation from carbon monoxide and/or carbon dioxide are strongly exothermic. In gas phase reactors, the strong exothermic reaction creates a zone  
10 with high temperature of typical around 280°C or higher within the catalyst tube, which promotes formation of by-products. The by-products formed are mainly higher alcohols such as ethanol, propanol, butanol and ketones. It is costly to separate these components from the methanol product due to the formation of azeotropes between ketones and  
15 methanol and ethanol and water. As a further disadvantage, the catalysts within the hot zones deactivate more rapidly. In the liquid phase reactor, the liquid phase reaction heat is absorbed in the liquid. The temperature can be better  
20 controlled and no hot zones are formed. Hence the formation of by-products is kept at a minimum.

Since heat removal is more efficient in the liquid phase process, mixtures of a wide range of gas compositions can  
25 be treated. The main advantage of the invention is that a CO-rich synthesis gas can be treated. Synthesis gas mixture compositions in the range of 15-30 vol.% CO, 60-74 vol.% hydrogen and 0.5-15 vol.% carbon dioxide have been treated. For a low content of carbon dioxide, the concentration of  
30 water in the methanol product will be low.

The process of the invention has the advantage of providing a high single-pass conversion. The high conversion is obtained because the conversion of methanol is not limited by thermodynamic equilibrium at condensing conditions as mentioned above.

The main advantage of the process is that a synthesis gas containing carbon dioxide can be processed. This is advantageous because it is expensive to produce a synthesis gas with low CO<sub>2</sub>.

When using the invented preparation method, cooling can take place by using cooling tubes producing medium or low-pressure steam. The tubes can be placed in the methanol/water slurry and this, together with agitation, ensures that the temperature is kept at an almost constant level. Circulation of liquid around the tubes ensures a good temperature distribution and control. In a tubular fixed-bed reactor, hot zones are usually formed in the centre of the catalyst tube since the reaction is very exothermic. This promotes by-product formation. The produced raw methanol can be used either as fuel methanol or fractionated into chemical grade methanol.

#### DETAILED DESCRIPTION OF THE INVENTION

By the invention methanol synthesis gas into a liquid phase, which consists of catalyst suspended in methanol, thereby reacting the synthesis gas to produce methanol. A small fraction of water can be tolerated (0-3 vol.%) in the methanol suspension without a significant deactivation of the catalyst.

The process can be operated as a once-through process and as a process in which unconverted gas is recycled.

5 The separation of the methanol product from the catalyst may be accomplished by inserting filters within the reactor. This will prevent the catalyst from leaving the reactor. Other systems would include filtration of the product or cyclone treatment outside the reactor.

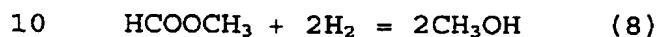
10 The synthesis gas is low in carbon dioxide giving a product with a low water content. Results have shown that the water production is around 0.02 g/g methanol.

15 The low water content confirms that the water gas shift reaction is active and that most of the produced water is consumed by this reaction.

The results also show that water can be tolerated in the present catalyst system. A water concentration of 0.55 wt%  
20 does not decrease the reaction rate to a high extent. The methanol product after reaction at for example 202°C and 116 bar in a once-through process consists of small amounts of water (1.64 wt%), DME (0.19 wt%), methyl formate (0.92 wt%), ethanol (0.29 wt%), acetic acid methyl ester (0.09 wt%) and carbonic acid di-methyl ester (0.06  
25 wt%). In addition, traces of acetone, methane dimethoxy, 1-propanol, formic acid (2-methyl ethyl ester) and carbonic acid dimethyl ester may be found (< 0.03 wt%).

30 The present innovation includes means for keeping the methyl formate concentration at a constant level in the reactor. Methyl formate can be separated from the methanol

product and recycled to the reactor. By recycling a methylformiate-rich stream to the reactor, chemical equilibrium will be established in the reactor and there will be no net production of methyl formiate. Example 7 illustrates the reduction of methyl formiate in the liquid phase from 35 mol% to 5 mol% at 200°C and 132 bar. At these conditions reactions (10) and (11) are shifted towards methanol production



In this case an activated commercial catalyst available from Haldor Topsøe A/S under the tradename MK-101P is used for methanol production. This is a Cu/Zn/Al-based catalyst. A number of other catalysts for methanol production may also be employed.

#### EXAMPLES

The following examples illustrate the results obtained with a batch process system. The composition of the gases that have been treated is given in Table 1.

Table 1

Synthesis gas composition

	Gas A [vol.%]	Gas B [vol.%]	Gas C [vol.%]	Gas D [vol.%]
H <sub>2</sub>	60.	74.	60.	60.
CO	30.	25.5	25.	15.
CO <sub>2</sub>	5.	0.5	5.	15.
N <sub>2</sub>	5.	0.	10.	10.
Total	100.	100.	100.	100.
H <sub>2</sub> /CO	2.0	3.0	2.4	4.
CO <sub>2</sub> /CO	0.17	0.02	0.2	1.

**Example 1**

A 120 ml autoclave reactor was loaded with active catalyst and methanol. Activated MK-101 (pulverised) is employed as catalyst. The autoclave was connected to a gas reservoir that contained a mixture of synthesis gas "A" comprising of hydrogen (60 vol.%), nitrogen (5 vol.%), carbon monoxide (30 vol.%) and carbon dioxide (5 vol.%) at 21°C and 162 bar. The volume of the gas reservoir was 0.5 l. The process was a closed batch system since neither gas nor liquid was removed from the system until the reaction was completed. The connection between the reactor and gas reservoir was opened. The reaction occurred in the autoclave at a constant pressure of 116 bar and a constant temperature of 202°C. The autoclave was agitated by stirring at 500 rpm. As the reaction proceeded, carbon dioxide and hydrogen were converted to methanol and water. The produced methanol and water condensed to liquid. Carbon monoxide reacted with water to produce hydrogen and carbon dioxide in the water gas shift reaction. The reactants were taken from the gas reservoir. The pressure drop in the gas reservoir was monitored and was used to determine the amount of gas consumed and hence the amount of methanol formed. With the pressure drop, the amount of methanol produced was calculated, assuming that reaction (7) resulted in the pressure drop. As the pressure in the gas reservoir had dropped to 121 bar, it was refilled to 162 bar and the reaction proceeded spontaneously until the gas reservoir pressure had dropped to 120 bar. Since the gas composition in the reactor changed with time, the reaction rate slowly decreased with time. A pressure drop corresponding to a gas consumption of 1.7



moles of synthesis gas resulted in 13.4 g of measured methanol product.

5 Table 2 illustrates the produced amount of methanol obtained for selected operating temperatures and pressures in the presented examples.

#### Example 2

10 Example 1 was repeated at a pressure of 109 bar and a temperature of 180°C, but with synthesis gas mixture "B" comprising of 74 vol.% hydrogen, 25.5 vol.% carbon monoxide and 0.5 vol.% carbon dioxide. A fresh catalyst suspension was employed with activated catalyst. The gas was taken from the gas reservoir at 21.2°C and a pressure of 168.9  
15 bar. Agitation was maintained at 500 rpm. Reaction continued spontaneously until a gas reservoir pressure of 130.6 bar. 6.3 g of methanol product was produced.

#### Example 3

20 Example 1 was repeated, at a pressure of 137 bar and a temperature of 200°C with the synthesis gas B from Example 2. The methanol suspension consisted of around 0.8 wt% of water originating from previous experiment. The same catalyst suspension was employed as in Example 2. The gas was taken  
25 from the reservoir at 170.4 bar at 21.6°C. The agitation rate was 500 rpm. At a reactor pressure of 131.4 bar, the reaction was terminated. The calculated product was 6.3 g.

**Table 2**  
Conditions for methanol production

Gas	Pressure (bar)	Temperature (°C)	$\Delta P$ (bar)	MeOH (g)
A	116	202	83.0	13.4
B	109	180	38.3	6.3
B	137	200	38.9	6.3
C	137	210	47.6	7.8
D	109	180	40.0	6.8

5

**Example 4**

Example 1 was repeated, but at a pressure of 137 bar and a temperature of 210°C with synthesis gas mixture "C" comprising of 60 vol.% hydrogen, 10 vol.% nitrogen, 25 vol.% carbon monoxide and 5 vol.% carbon dioxide. The same suspension had been used for 5 previous experiments. The gas was taken from the gas reservoir at 21.2°C and a pressure of 168 bar. Agitation was maintained at 500 rpm. The gas reservoir pressure dropped to 138.4 bar and the reservoir was refilled to 167 bar. Reaction continued spontaneously to a gas reservoir pressure of 149 bar. 7.8 g of methanol product was produced.

10

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**Example 5**

Example 1 was repeated, but at a pressure of 109 bar and a temperature of 180°C with synthesis gas mixture "D" comprising of 60 vol.% hydrogen, 10 vol.% nitrogen, 15 vol.% carbon monoxide and 15 vol.% carbon dioxide. The catalyst suspension had been used in previous experiments. The gas was taken from the gas reservoir at 21.3°C and a pressure of 162 bar. Agitation was maintained at 500 rpm. Reaction

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continued spontaneously until a reservoir pressure of 122 bar. 6.8 g of methanol was produced.

#### **Example 6**

##### 5 Influence of water concentration.

The influence of water concentration was investigated. The results are listed in Table 3.

##### 10 (6a) Methanol solution of <0.05 wt% water

Fresh activated catalyst was employed in a methanol suspension of below 0.05 wt% water. The synthesis gas B was added at the operating conditions of 138 bar and 200°C. The gas was taken from the gas reservoir at 19.5°C and a pressure of 167 bar. The pressure dropped to 137 bar in the reservoir. The reservoir was refilled twice to 166 bar. The pressure drop was 30.2, 21.4 and 4 bar, respectively, in each period. 9.1 g of methanol was produced. The water concentration in methanol after the experiment was 0.48 wt%.

20

##### (6b) Methanol solution of 5 wt% water

Example 6a was repeated but at 139 bar and 200°C re-using the same catalyst as used in Example 6a. Water was added to an initial concentration of 5 wt% in methanol. The pressure drop was in total 48.3 bar, and 7.9 g of methanol was produced. The water concentration in methanol after the experiment was 3.6 wt%.

25

##### (6c) Methanol solution of 9 wt% water

Example 6a was repeated at 141 bar and 200°C re-using the same catalyst as used in Examples 6a and 6b. Water was added to an initial concentration of 9 wt% in methanol. The

30

pressure drop was in total 47.8 bar and 7.8 g of methanol was produced. The water concentration after the experiment was 7.6 wt%.

5

**Table 3**

Methanol production in presence of water for gas B

P (bar)	T (°C)	[H <sub>2</sub> O] wt%	ΔP (bar)	MeOH (g)
138	200	< 0.05	55.6	9.1
139	200	5	48.3	7.9
141	200	9	47.8	7.8

10

**Example 7**

Reduction of methyl formiate concentration.

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This example illustrates that the concentration of the abundant by-product methyl formiate can be reduced significantly by chemical equilibrium between hydrogen, carbon monoxide, methyl formiate and methanol in reaction (7) and (8). Hence, if a methyl-formiate-rich stream is recycled to the reactor, there will be no net production of methyl formiate in the reactor.

20

25

The experiment was run with an initial concentration of 34.8 mole% methyl formiate in a methanol suspension. The experiment was carried out at 200°C and 132 bar using the same procedure as in the examples above. At 132 bar and 200°C, reactions (1) and (2) are shifted towards methanol production. Fresh, activated catalyst was employed. The hydrogen-rich synthesis gas B was used. The pressure drop in the reservoir was 29 bar. The final concentration of methyl

formiate was reduced to 5.4 mole% in the liquid phase. This corresponds to an analysed exit dry gas concentration of hydrogen of around 24 mole%.

5

**Table 4**

Liquid concentration of MF and methanol  
before and after experiment

Component	$X_L$ [mole %] start	$X_L$ [mole %] end
Methyl formiate	34.8	5.4
Methanol	65.2	94.6

## CLAIMS

1. A process for preparing methanol from a synthesis gas comprising carbon monoxide, carbon dioxide and hydrogen by steps of:
  - (a) passing the synthesis gas into a reactor containing a solid methanol conversion catalyst suspended in a liquid phase of methanol and water;
  - (b) reacting the synthesis gas in presence of the suspended catalyst at a pressure and temperature, where methanol being formed on the catalyst condenses into the liquid phase; and
  - (c) withdrawing from the reactor a part of the liquid phase containing formed methanol product.
2. A process in accordance with claim 1, wherein amount of water being present in the liquid phase is 0-10 wt%, preferably 0-3 wt%.
3. A process in accordance with claim 1, wherein the pressure in the slurry bed reactor is 50-290 bar, preferentially 60-140 bar.
4. A process in accordance with claim 1, wherein the temperature in the slurry bed reactor is between 150°C to 240 °C, preferentially 180-225°C.
5. A process in accordance with claim 1, wherein the synthesis gas has a CO<sub>2</sub>/CO molar ratio of 0.02-1.0 and an H<sub>2</sub>/CO molar ratio of 2-4.

6. A process in accordance with claim 1, wherein the synthesis gas comprises 15-35 vol.% CO, 60-74 vol.% H<sub>2</sub> and 0-15 vol.% CO<sub>2</sub>.
- 5 7. A process of claims 1 further comprising of a step of recycling an effluent gas stream being withdrawn from the reactor.
8. A process of claim 1, wherein the reacting synthesis gas is cooled by internal cooling means.  
10
9. A process of claim 1, wherein methanol and/or catalyst is added as fresh or being recycled to the reactor.
- 15 10. A process according to any one of the preceding claims, wherein a stream comprising methanol and by-products including methyl formiate is recycled to the reactor.

**ABSTRACT**

The present invention is a novel process for methanol production in a liquid phase reactor from a synthesis gas comprising of hydrogen, carbon dioxide and carbon monoxide. 5 The liquid phase reactor contains a solid catalyst suspended in methanol. In this innovation, methanol acts both as a product and as a suspension medium for the catalyst. The new innovation exploits the condensing conditions for 10 methanol production. By operating at condensing conditions, the methanol partial pressure at equilibrium is higher than the boiling pressure of methanol at the given temperature. Hence the produced methanol of the equilibrium composition condenses creating the potential of more gas to be converted. 15 Since equilibrium is not a limiting factor, high conversions can be obtained.



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FIGURE

